Mapping Approach for Quantum-Classical Time Correlation Functions

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Abstract

The calculation of quantum canonical time correlation functions is considered in this paper. Transport properties, such as diffusion and reaction rate coefficients, can be determined from time integrals of these correlation functions. Approximate, quantum-classical expressions for correlation functions, which are amenable to simulation, are derived. These expressions incorporate the full quantum equilibrium structure of the system but approximate the dynamics by quantum-classical evolution where a quantum subsystem is coupled to a classical environment. The main feature of the formulation is the use of a mapping basis where the subsystem quantum states are represented by fictitious harmonic oscillator states. This leads to a full phase space representation of the dynamics that can be simulated without appeal to surface-hopping methods. The results in this paper form the basis for new simulation algorithms for the computation of quantum transport properties of large many-body systems.

1 Introduction

In the investigation of condensed phase systems one is usually interested in the average value of some observable or in a time correlation function from which a transport coefficient can be computed. Since the basic description of matter is quantum mechanical, we are interested in the average value of a quantum mechanical operator, which is given by $\overline{B(t)} = \text{Tr}\hat{B}(t)\hat{\rho}(0)$, where, for a system with Hamiltonian $\hat{H}$, the time dependent operator satisfies the Heisenberg equation of motion,

$$\frac{d}{dt}\hat{B}(t) = \frac{i}{\hbar}[\hat{H}, \hat{B}], \tag{1}$$

and $\hat{\rho}(0)$ is the initial value of the density matrix. Quantum time correlation functions of two operators, $\hat{A}$ and $\hat{B}$ have the form[1], $C_{AB}(t) = \text{Tr}(\hat{\rho}_{\text{eq}}\hat{A}\hat{B}(\text{t}))$, where $\hat{\rho}_{eq}$ is the quantum canonical equilibrium density matrix. Either of these quantum expressions requires a knowledge of the time evolution of a quantum operator in a many-body system that is often very large. Consequently, these general expressions are not computationally tractable and appeal must be made to approximations if they are to be evaluated for problems of physical interest.

The approximate dynamical description we consider in this paper is quantum-classical Liouville dynamics [2]. In this formulation the system is partitioned into two subsystems, which we call quantum

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[1]Other forms of quantum correlation functions are useful in applications. These include symmetrized and Kubo transformed forms. Since relations exist among these correlation functions [1], we restrict our considerations to this expression.

subsystem and bath or environment. The partition is dictated by physical principles. For example, in electron or proton transfer problems, the electron or proton may constitute the quantum subsystem while the environment in which the transfer takes place, a molecular group or biomolecule dissolved in a solvent, forms the bath. In quantum-classical Liouville dynamics the bath is treated classically while retaining the full quantum character of the quantum subsystem. In this theory the analog of the Heisenberg equation of motion for an operator is [2, 3]

$$\frac{d}{dt}\hat{B}_W(X,t) = \frac{i}{\hbar}[\hat{H}_W, \hat{B}_W] - \frac{1}{2}(\{\hat{H}_W, \hat{B}_W\} - \{\hat{B}_W, \hat{H}_W\}),\tag{2}$$

where $X = (R, P)$ are the positions and momenta of the bath degrees of freedom. The subscript W indicates that operators are expressed in a partial Wigner representation defined below. In addition to the usual quantum commutator, the equation of motion also involves a Poissson bracket denoted by $\{\cdot, \cdot\}$. While this equation is far more tractable than the full quantum equations of motion, its numerical simulation presents challenges and a number of different schemes have been constructed for this purpose [4, 5]. These include Trotter-based methods that use an adiabatic basis [6], as well as trajectory methods that use the diabatic [7] and force bases [8], schemes based on the multiple threads algorithm [9] and a method that utilizes the mapping basis [10]. The mapping method has proved to be especially promising for the evaluation of expectation values of operators, as shown by calculations of population relaxation in the spin-boson model, one of the standard test cases for quantum dynamics [10]. In this paper, we show how the mapping method can be extended to the computation of time correlation functions within the quantum-classical Liouville framework.

In the next section, we present the explicit expression for the quantum correlation function that forms the basis of our calculations. Section 3 outlines the mapping formulation where subsystem quantum states are replaced by fictitious harmonic oscillator states. Section 4 reformulates the quantum correlation function in the mapping basis. This fully quantum description is exact and the dynamics is embodied in the spectral density function. A quantum-classical approximation for the spectral density dynamics is derived in Sec. 5. The details of this derivation are presented in the Appendix. This result is used in Sec. 6 to obtain the final result for the quantum-classical correlation function in the mapping basis. The conclusions of the study are presented in Sec. 7.

2 Correlation Function

Before considering quantum-classical approximations to the dynamics, we first rewrite the exact quantum correlation function in a form that is suitable for the introduction of the mapping basis and passage to the quantum-classical limit. Suppose the quantum subsystem and bath have N_s and N_b degrees of freedom with characteristic masses m and M, respectively. In order to introduce a phase space description of the bath, we first introduce a coordinate representation of the bath so that the correlation function takes the form,

$$
\begin{aligned}
C_{AB}(t) &= \operatorname{Tr}(\hat{\rho}_{\mathrm{eq}}\hat{A}\hat{B}(t)) = \operatorname{Tr}(\hat{\rho}_{\mathrm{eq}}\hat{A}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}) \\
&= \operatorname{Tr}' \int dQ_1 dQ_2 dQ_3 dQ_4 \langle Q_1|\hat{\rho}_{\mathrm{eq}}\hat{A}|Q_2\rangle\langle Q_2|e^{i\hat{H}t/\hbar}|Q_3\rangle\langle Q_3|\hat{B}|Q_4\rangle\langle Q_4|e^{-i\hat{H}t/\hbar}|Q_1\rangle \\
&= \operatorname{Tr}' \int dR_1 dR_2 dZ_1 dZ_2 \langle R_1 - \frac{Z_1}{2}|\hat{\rho}_{\mathrm{eq}}\hat{A}|R_1 + \frac{Z_1}{2}\rangle\langle R_1 + \frac{Z_1}{2}|e^{i\hat{H}t/\hbar}|R_2 - \frac{Z_2}{2}\rangle \\
&\quad \times \langle R_2 - \frac{Z_2}{2}|\hat{B}|R_2 + \frac{Z_2}{2}\rangle\langle R_2 + \frac{Z_2}{2}|e^{-i\hat{H}t/\hbar}|R_1 - \frac{Z_1}{2}\rangle.
\end{aligned}\tag{3}
$$

In these equations, Tr' stands for a trace over the quantum subsystem degrees of freedom and, in the forth equality above, we have made a change of variables $Q_1 = R_1 - Z_1/2$, $Q_2 = R_1 + Z_1/2$, etc.

Two further manipulations are required to cast the correlation function into a form that is suitable for the calculations using the mapping basis described below. The coordinate space matrix elements may be replaced with bath phase space functions by introducing the partial [3] Wigner transforms [11, 12, 13] of an operator and density matrix,

$$\langle R - \frac{Z}{2}|\hat{B}|R + \frac{Z}{2}\rangle = \frac{1}{(2\pi\hbar)^{N_b}} \int dP \hat{B}_W(R,P)e^{-iP\cdot Z/\hbar},$$

$$\langle R - \frac{Z}{2}|\hat{\rho}_{eq}\hat{A}|R + \frac{Z}{2}\rangle = \int dP (\hat{\rho}_{eq}\hat{A})_W(R,P)e^{-iP\cdot Z/\hbar}. \qquad (4)$$

Note that the partially Wigner transformed quantities are still operators in the quantum subsystem Hilbert space. In addition, Tr' may be written explicitly using the eigenfunctions of the Hamiltonian of the quantum subsystem. The Hamiltonian for the entire system is given by

$$\hat{H} = \frac{\hat{P}^2}{2M} + \hat{V}_b(\hat{R}) + \frac{\hat{p}^2}{2m} + \hat{V}_s(\hat{q}) + \hat{V}_c(\hat{R},\hat{q}), \qquad (5)$$

where $\hat{P}$ and $\hat{p}$ are momentum operators of the bath and subsystem and $\hat{V}_b$, $\hat{V}_s$ and $\hat{V}_c$ are, respectively, the bath, subsystem and coupling potentials. The coordinate operators for the subsystem and bath are $\hat{q}$ and $\hat{R}$, respectively. Equation (5) can be written as $\hat{H} = \frac{\hat{P}^2}{2M} + \hat{V}_b + \hat{V}_c + \hat{h}_s$, where $\hat{h}_s = \frac{\hat{p}^2}{2m} + \hat{V}_s$ is the subsystem Hamiltonian. The eigenstates of $\hat{h}_s$ are defined by the eigenvalue problem $\hat{h}_s|\lambda\rangle = \epsilon_\lambda|\lambda\rangle$. We suppose that there are N quantum subsystem states. Making use of subsystem energy eigenstates as a basis and introducing the Wigner transformed forms of $\hat{\rho}_{eq}\hat{A}$ and $\hat{B}$ given in Eq. (4) we have,

$$C_{AB}(t) = \frac{1}{(2\pi\hbar)^{N_b}} \sum_{\lambda,\lambda',\mu,\mu'=1}^{N} \int dX_1 dX_2 dZ_1 dZ_2 \, \langle\lambda|(\hat{\rho}_{eq}\hat{A})_W(X_1)|\lambda'\rangle$$

$$\times \langle\lambda'|\langle R_1 + \frac{Z_1}{2}|e^{i\hat{H}t/\hbar}|R_2 - \frac{Z_2}{2}\rangle|\mu\rangle\langle\mu|\hat{B}_W(X_2)|\mu'\rangle$$

$$\times \langle\mu'|\langle R_2 + \frac{Z_2}{2}|e^{-i\hat{H}t/\hbar}|R_1 - \frac{Z_1}{2}\rangle|\lambda\rangle e^{-\frac{i}{\hbar}(P_1\cdot Z_1 + P_2\cdot Z_2)}. \qquad (6)$$

The spectral density function in the subsystem basis may be defined as

$$W^{\lambda'\lambda\mu'\mu}(X_1,X_2,t) = \int dZ_1 dZ_2 \, \langle\lambda'|\langle R_1 + \frac{Z_1}{2}|e^{i\hat{H}t/\hbar}|R_2 - \frac{Z_2}{2}\rangle|\mu\rangle$$

$$\times \langle\mu'|\langle R_2 + \frac{Z_2}{2}|e^{-i\hat{H}t/\hbar}|R_1 - \frac{Z_1}{2}\rangle|\lambda\rangle e^{-\frac{i}{\hbar}(P_1\cdot Z_1 + P_2\cdot Z_2)}, \qquad (7)$$

and contains all information needed to compute the quantum time evolution contribution to the correlation function. The spectral density defined via full Wigner transform was used by Filinov *et al.* [14, 15, 16] in a reformulation of the quantum correlation function. In terms of the spectral density function in the subsystem basis the correlation function takes the form,

$$C_{AB}(t) = \frac{1}{(2\pi\hbar)^{N_b}} \sum_{\lambda,\lambda',\mu,\mu'}^{N} \int dX_1 dX_2 \, \langle\lambda|(\hat{\rho}_{eq}\hat{A})_W(X_1)|\lambda'\rangle\langle\mu|\hat{B}_W(X_2)|\mu'\rangle W^{\lambda'\lambda\mu'\mu}(X_1,X_2,t). \qquad (8)$$

This expression for the quantum correlation function is exact. In order to compute it, the matrix elements of the forward and backward propagators must be evaluated to solve for the time dependence of the spectral density function. This is the most difficult part of the problem. A similar expression utilizing the adiabatic basis in place of the subsystem basis was derived earlier [17]. In addition to the time dependent spectral density function, the time independent matrix elements of the quantum operators and quantum equilibrium density matrix must also be computed to evaluate the ensemble average appearing in the definition of the correlation function. While these equilibrium quantities may be difficult to evaluate for complex systems, they are far easier to compute than the quantum time dependence, and algorithms have been developed for this purpose [18, 19].

3 Mapping Basis

In order to construct a useful simulation algorithm for the quantum correlation function, it is convenient to use an alternative, but equivalent, mapping form for the quantum subsystem matrix elements of the operators which enter in its definition. A well-known mapping approach was introduced by Schwinger [20]. In his scheme, the eigenstates of the angular momentum operator are mapped onto eigenfunctions of two bosonic oscillators, and the angular momentum operators are mapped onto combinations of creation, $\hat{a}_\lambda^\dagger$, and annihilation, $\hat{a}_{\lambda'}$, operators ($\lambda, \lambda' = 1$ or 2). Such a mapping yields a simple treatment of the angular momentum problem in quantum mechanics. In this formalism the resolution of identity is mapped to $\hat{a}_1^\dagger \hat{a}_1 + \hat{a}_2^\dagger \hat{a}_2 = 1$. This equality is used in the Holstein-Primakoff mapping scheme to eliminate one bosonic oscillator and represent angular momentum states by a single oscillator [21]. An extension of these mapping schemes was used to map discreet states of a quantum system onto fictitious harmonic oscillators, so that all degrees of freedom in the system can be treated with semiclassical approximations [22, 23, 24, 25, 26, 27, 28]. The mapping approach has also been used in other closely related contexts [29, 30, 31].

In the mapping scheme used in this work, an N level quantum system is mapped onto N harmonic oscillators. The wavefunction of the system in a given quantum state is mapped onto a product of harmonic oscillator wavefunctions where all oscillators are in their ground state, except for one oscillator corresponding to the given quantum state, which is in its first excited state. This mapping is schematically represented in Fig 1. Therefore, we have a physical space with a cardinality N, which is much lower than the cardinality of the Hilbert space of the N harmonic oscillators, which is infinite. More specifically, the subsystem quantum states are mapped through the relations

$$|\lambda\rangle \to |m_\lambda\rangle = |0_1, \cdots, 1_\lambda, \cdots, 0_N\rangle, \qquad (9)$$

where

$$\langle q|m_\lambda\rangle = \langle q_1, q_2, \cdots, q_N|0_1, \cdots, 1_\lambda, \cdots, 0_N\rangle = \phi_0(q_1)\cdots\phi_0(q_{\lambda-1})\phi_1(q_\lambda)\cdots\phi_0(q_N),$$

with ϕ_0 and ϕ_1, respectively, being the ground and the first excited state wavefunctions of an harmonic oscillator. The creation and annihilation operators on the mapping states act in the following ways[2]:

$$\hat{a}_\lambda^\dagger|0\rangle = |0_1, \cdots, 1_\lambda, \cdots, 0_N\rangle = |m_\lambda\rangle, \qquad \text{and} \qquad \hat{a}_\lambda|m_\lambda\rangle = |0_1, \cdots, 0_N\rangle = |0\rangle, \qquad (10)$$

where

$$\hat{a}_\lambda = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{q}_\lambda + \frac{i}{m\omega}\hat{p}_\lambda\right), \qquad \hat{a}_\lambda^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{q}_\lambda - \frac{i}{m\omega}\hat{p}_\lambda\right), \qquad \text{and} \qquad [\hat{q}_\lambda, \hat{p}_\lambda] = i\hbar. \qquad (11)$$

We may then introduce the mapping representation of an operator $\hat{A}$ as

$$\hat{A}_m = \sum_{\lambda\lambda'} A_{\lambda\lambda'}\hat{a}_\lambda^\dagger \hat{a}_{\lambda'}. \qquad (12)$$

For example, the mapping form of the Hamiltonian in Eq. (5) is

$$
\begin{aligned}
\hat{H}_m &= \sum_{\lambda\lambda'}\left[\frac{\hat{P}^2}{2M}\delta_{\lambda\lambda'} + \hat{V}_B(\hat{R})\delta_{\lambda\lambda'} + h_{\lambda\lambda'}(\hat{R})\right]\hat{a}_\lambda^\dagger \hat{a}_{\lambda'} \\
&= \frac{\hat{P}^2}{2M} + \hat{V}_B(\hat{R}) + \frac{m\omega}{2\hbar}\sum_{\lambda\lambda'} h_{\lambda\lambda'}(\hat{R})\left(\hat{r}_\lambda\hat{r}_{\lambda'} + \frac{\hat{p}_\lambda\hat{p}_{\lambda'}}{m^2\omega^2} - \frac{\hbar}{m\omega}\delta_{\lambda\lambda'}\right),
\end{aligned}
\qquad (13)
$$

---

[2]Since the harmonic oscillators are fictitious we may set $m\omega$ to 1 to simplify these expressions; however, we retain these forms both to make dimensional consistency manifest and to simplify the dynamical relations (see Sec. 5) by equating m to the quantum subsystem characteristic mass and ω to the inverse of the scaling time.
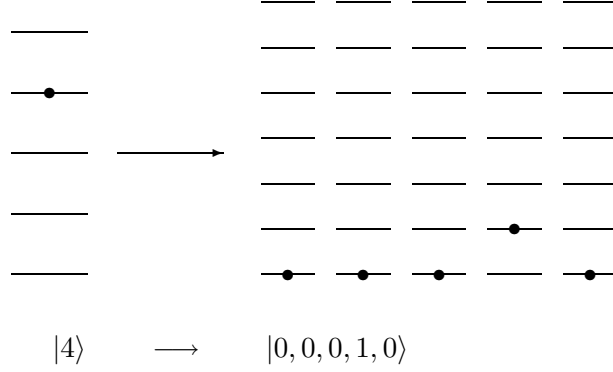
Figure 1: Schematic representation of the mapping for a 5 level system. Subsystem states are on the left and the mapping states are on the right.

where $\hat{h} = \frac{\hat{p}^2}{2m} + \hat{V}_s(\hat{q}) + \hat{V}_c(R, \hat{q})$ and $h_{\lambda\lambda'}$ is its matrix element. We used the fact that $h_{\lambda\lambda'} = h_{\lambda'\lambda}$ in writing this expression. Note that unlike Eq. (5) where $\hat{q}$ and $\hat{p}$ are the subsystem coordinates and momenta, in Eq. (13) $\hat{r}$ and $\hat{p}$ are the mapping space coordinates and momenta. These quantities have dimensions equal to the number of subsystem quantum states.

From the definition in Eq. (12) it is clear that the matrix elements of $\hat{A}$ in the subsystem basis are identical to those of $\hat{A}_m$ in the mapping basis: $\langle\lambda|\hat{A}|\lambda'\rangle = A_{\lambda\lambda'} = \langle m_\lambda|\hat{A}_m|m_{\lambda'}\rangle$. Consequently, any matrix element in the quantum subsystem basis can be substituted by its equivalent form in the mapping basis. We show that this substitution leads to computational advantages when simulating quantum correlation functions.

4   Correlation Function in Mapping Basis

The matrix elements in the correlation function expression (6) can be replaced by their mapping equivalent forms to yield

$$
\begin{aligned}
C_{AB}(t) &= \frac{1}{(2\pi\hbar)^{N_b}} \sum_{\lambda\lambda'\mu\mu'=1}^{N} \int dX_1 dX_2 dZ_1 dZ_2 \, \langle m_\lambda|(\hat{\rho}_{eq}\hat{A})_{Wm}(X_1)|m_{\lambda'}\rangle \\
&\times \langle m_{\lambda'}|\langle R_1 + \frac{Z_1}{2}|e^{i\hat{H}_m t/\hbar}|R_2 - \frac{Z_2}{2}\rangle|m_\mu\rangle\langle m_\mu|\hat{B}_{Wm}(X_2)|m_{\mu'}\rangle \\
&\times \langle m_{\mu'}|\langle R_2 + \frac{Z_2}{2}|e^{-i\hat{H}_m t/\hbar}|R_1 - \frac{Z_1}{2}\rangle|m_\lambda\rangle e^{-\frac{i}{\hbar}(P_1 \cdot Z_1 + P_2 \cdot Z_2)}.
\end{aligned}
\tag{14}
$$

The next step in the analysis of this correlation function is to introduce a coordinate space representation of the abstract mapping eigenfuctions. Inserting resolutions of the identity, $\int dq\,|q\rangle\langle q| = 1$ and making use of the closure relation for mapping states, $\sum_\lambda \langle q'|m_\lambda\rangle\langle m_\lambda|q\rangle = \delta(q - q')$, the correlation function takes the form

$$
\begin{aligned}
C_{AB}(t) &= \frac{1}{(2\pi\hbar)^{N_b}} \int dX_1 dX_2 dZ_1 dZ_2 dq_1 dq_2 dq_4 dq_6 \, \langle q_1|(\hat{\rho}_{eq}\hat{A})_{Wm}(X_1)|q_2\rangle \\
&\times \langle q_2|\langle R_1 + \frac{Z_1}{2}|e^{i\hat{H}_m t/\hbar}|R_2 - \frac{Z_2}{2}\rangle|q_4\rangle\langle q_4|\hat{B}_{Wm}(X_2)|q_6\rangle \\
&\times \langle q_6|\langle R_2 + \frac{Z_2}{2}|e^{-i\hat{H}_m t/\hbar}|R_1 - \frac{Z_1}{2}\rangle|q_1\rangle e^{-\frac{i}{\hbar}(P_1 \cdot Z_1 + P_2 \cdot Z_2)}.
\end{aligned}
\tag{15}
$$

5

It is important to note that the dimensionality of the mapping coordinate space representation is fixed by the number of quantum states.

A phase space description of this coordinate representation can be obtained by introducing Wigner transforms of the matrix elements. Making the change of variables, $q_1 = r_1 - z_1/2$, $q_2 = r_1 + z_1/2$, etc., and, using the analog of Eq. (4) for the mapping coordinates, we find

$$
\begin{aligned}
C_{AB}(t) &= \frac{1}{(2\pi\hbar)^{(N_b+N)}} \int dX_1 dX_2 dx_1 dx_2 \, (\hat{\rho}_{eq}\hat{A})_{Wm}(X_1, x_1) \\
&\times B_{Wm}(X_2, x_2) W(X_1, X_2, x_1, x_2, t),
\end{aligned} \tag{16}
$$

where, in analogy with the bath phase space terminology, $x = (r, p)$. The full Wigner representation of the mapping spectral density, W, is defined as

$$
\begin{aligned}
W(X_1, X_2, x_1, x_2, t) = \int dZ_1 dZ_2 dz_1 dz_2 \, \langle r_1 + \frac{z_1}{2}|\langle R_1 + \frac{Z_1}{2}|e^{i\hat{H}_m t/\hbar}|R_2 - \frac{Z_2}{2}\rangle|r_2 - \frac{z_2}{2}\rangle \\
\times \langle r_2 + \frac{z_2}{2}|\langle R_2 + \frac{Z_2}{2}|e^{-i\hat{H}_m t/\hbar}|R_1 - \frac{Z_1}{2}\rangle|r_1 - \frac{z_1}{2}\rangle e^{-\frac{i}{\hbar}(P_1 \cdot Z_1 + P_2 \cdot Z_2 + p_1 \cdot z_1 + p_2 \cdot z_2)}. \quad (17)
\end{aligned}
$$

All of these manipulations have served simply to cast the exact expression for the quantum correlation function into an equivalent exact form involving a phase-space-like representation for both the bath and the mapping version of the quantum subsystem degrees of freedom. There are advantages to defining W and deriving its dynamics rather than directly considering the dynamics of the correlation function. Not only are the algebraic manipulations simplified, but also all correlation functions for a specific system share the same spectral density. This fully quantum problem is still intractable for complex many-body systems. We now turn to the evaluation of the spectral density function in the quantum-classical limit that will provide the basis for simulation algorithms of the dynamics.

5 Quantum-Classical Dynamics for W

Given the development presented above, the dynamical problem consists in finding a tractable equation of motion for the spectral density function $W(X_1, X_2, x_1, x_2, t)$ and constructing an algorithm for its solution. The equation of motion can be derived by differentiating W with respect to time. However, to derive the quantum-classical equation for W we must introduce approximations. For this purpose we make use of an expansion in the small mass ratio $\mu = (m/M)^{1/2}$, where it is assumed that the characteristic mass M of the bath particles is much larger than m for the quantum subsystem particles. The manner in which this expansion is carried out is analogous to that discussed earlier for quantum Liouville equation [3]. More specifically, given the energy ϵ_0, time $t_0 = \hbar/\epsilon_0$, and length $\lambda_m = (\hbar^2/m\epsilon_0)^{1/2}$ units, we scale the light and heavy particle momenta, respectively, with $p_m = (m\lambda_m/t_0) = (m\epsilon_0)^{1/2}$ and $P_M = (M\epsilon_0)^{1/2}$. Note that the only difference between subsystem and bath particles is scaling their momenta with different factors. As the subsystem and bath are in thermal equilibrium their average kinetic energies are equal and therefore, on average, $p/P = \mu$, so that after scaling both subsystem and bath momenta have the same order of magnitude. After scaling variables, we obtain

$$
\begin{aligned}
W'(R_1', P_1', R_2', P_2', r_1', p_1', r_2', p_2'; t') = \int dZ_1' dZ_2' dz_1' dz_2' \langle r_1' + \frac{z_1'}{2}|\langle R_1' + \frac{Z_1'}{2}|e^{i\hat{H}'_m t'}|R_2' - \frac{Z_2'}{2}\rangle|r_2' - \frac{z_2'}{2}\rangle \\
\times \langle r_2' + \frac{z_2'}{2}|\langle R_2' + \frac{Z_2'}{2}|e^{-i\hat{H}'_m t'}|R_1' - \frac{Z_1'}{2}\rangle|r_1' - \frac{z_1'}{2}\rangle e^{-i\mu^{-1}(P_1' \cdot Z_1' + P_2' \cdot Z_2')} e^{-i(p_1' \cdot z_1' + p_2' \cdot z_2')}, \quad (18)
\end{aligned}
$$

where a prime means that the variable is divided by the corresponding scaling factor. To avoid cumbersome notation, we drop the primes in the following relations. Differentiation of the scaled form of

W yields the equation of motion,

$$
\begin{aligned}
\frac{\partial W(t)}{\partial t} &= i \int dZ_1 dZ_2 dz_1 dz_2 dQ dq \left[\langle r_1 + \frac{z_1}{2} | \langle R_1 + \frac{Z_1}{2} | \hat{H}_m | Q \rangle | q \rangle \right. \\
&\quad \times \langle q | \langle Q | e^{i\hat{H}_m t} | R_2 - \frac{Z_2}{2} \rangle | r_2 - \frac{z_2}{2} \rangle \langle r_2 + \frac{z_2}{2} | \langle R_2 + \frac{Z_2}{2} | e^{-i\hat{H}_m t} | R_1 - \frac{Z_1}{2} \rangle | r_1 - \frac{z_1}{2} \rangle \\
&\quad - \langle r_1 + \frac{z_1}{2} | \langle R_1 + \frac{Z_1}{2} | e^{i\hat{H}_m t} | R_2 - \frac{Z_2}{2} \rangle | r_2 - \frac{z_2}{2} \rangle \langle r_2 + \frac{z_2}{2} | \langle R_2 + \frac{Z_2}{2} | e^{-i\hat{H}_m t} | Q \rangle | q \rangle \\
&\quad \left. \times \langle Q | \langle q | \hat{H}_m | R_1 - \frac{Z_1}{2} \rangle | r_1 - \frac{z_1}{2} \rangle \right] e^{-i\mu^{-1}(P_1 \cdot Z_1 + P_2 \cdot Z_2)} e^{-i(p_1 \cdot z_1 + p_2 \cdot z_2)}.
\end{aligned} \tag{19}
$$

The mapping Hamiltonian (Eq. (13)) in scaled variables is $\hat{H}_m = \frac{\hat{P}^2}{2} + \hat{V}_B(\hat{R}) + \sum_{\lambda\lambda'} \frac{h_{\lambda\lambda'}(\hat{R})}{2}(\hat{r}_\lambda \hat{r}_{\lambda'} + \hat{p}_\lambda \hat{p}_{\lambda'} - \delta_{\lambda\lambda'})$, while the scaled quantum mechanical momentum operators are $\hat{P} = \frac{\mu}{i} \frac{\partial}{\partial Q}$ and $\hat{p} = -i \frac{\partial}{\partial q}$. Substituting the Hamiltonian and momentum operators into Eq. (19) yields,

$$
\begin{aligned}
\frac{\partial W(t)}{\partial t} &= i\mu^{2N_b} \int d\tilde{Z}_1 d\tilde{Z}_2 dQ dz_1 dz_2 dq\, e^{-i(P_1 \tilde{Z}_1 + P_2 \tilde{Z}_2)} e^{-i(p_1 \cdot z_1 + p_2 \cdot z_2)} \\
&\quad \times \left\{ \left\{ \left[\frac{-\mu^2}{2} \frac{\partial^2}{\partial Q^2} + V_B(Q) + \frac{1}{2} \sum_{\lambda\lambda'} h_{\lambda\lambda'}(Q)(q_\lambda q_{\lambda'} - \frac{\partial}{\partial q_\lambda} \frac{\partial}{\partial q_{\lambda'}} - \delta_{\lambda\lambda'}) \right] \right. \right. \\
&\quad \times \delta(Q - R_1 - \frac{\mu \tilde{Z}_1}{2}) \delta(q - r_1 - \frac{z_1}{2}) \right\} \langle q | \langle Q | e^{i\hat{H}_m t} | R_2 - \frac{\mu \tilde{Z}_2}{2} \rangle | r_2 - \frac{z_2}{2} \rangle \\
&\quad \times \langle r_2 + \frac{z_2}{2} | \langle R_2 + \frac{\mu \tilde{Z}_2}{2} | e^{-i\hat{H}_m t} | R_1 - \frac{\mu \tilde{Z}_1}{2} \rangle | r_1 - \frac{z_1}{2} \rangle \\
&\quad - \left\{ \left[\frac{-\mu^2}{2} \frac{\partial^2}{\partial Q^2} + V_B(Q) + \frac{1}{2} \sum_{\lambda\lambda'} h_{\lambda\lambda'}(Q)(q_\lambda q_{\lambda'} - \frac{\partial}{\partial q_\lambda} \frac{\partial}{\partial q_{\lambda'}} - \delta_{\lambda\lambda'}) \right] \right. \\
&\quad \times \delta(Q - R_1 + \frac{\mu \tilde{Z}_1}{2}) \delta(q - r_1 + \frac{z_1}{2}) \right\} \langle r_1 + \frac{z_1}{2} | \langle R_1 + \frac{\mu \tilde{Z}_1}{2} | e^{i\hat{H}_m t} | R_2 - \frac{\mu \tilde{Z}_2}{2} \rangle | r_2 - \frac{z_2}{2} \rangle \\
&\quad \left. \times \langle r_2 + \frac{z_2}{2} | \langle R_2 + \frac{\mu \tilde{Z}_2}{2} | e^{-i\hat{H}_m t} | Q \rangle | q \rangle \right\},
\end{aligned} \tag{20}
$$

where the change of variable $\tilde{Z}_1 = Z_1/\mu$ was performed in order to transfer the μ dependence from the exponential to the argument of the potential energy terms, after integrations over Q and q have been performed. It is more convenient to expand a potential energy term around a small argument rather than to deal with an oscillatory exponential.

We begin the calculation by performing the integrals over q and Q, followed by Taylor expansion of the potential energy terms around $\mu = 0$, keeping terms up to the first order in μ. Finally, we introduce the definition of W into the resulting expression. The algebra is lengthy so it is presented in the Appendix. While the algebra leading to the result is lengthy, the final equation of motion is relatively simple. In unscaled coordinates it takes the form,

$$
\begin{aligned}
\frac{\partial W(t)}{\partial t} &= -\frac{1}{\hbar} \sum_{\lambda\lambda'} h_{\lambda\lambda'}(R_1) \left[r_{1\lambda} \frac{\partial}{\partial p_{1\lambda'}} - p_{1\lambda} \frac{\partial}{\partial r_{1\lambda'}} \right] W(t) + \left(\frac{P_1}{M} \cdot \frac{\partial}{\partial R_1} - \frac{\partial H_m}{\partial R_1} \cdot \frac{\partial}{\partial P_1} \right) W(t) \\
&\quad + \frac{\hbar}{8} \sum_{\lambda\lambda'} \frac{\partial h_{\lambda\lambda'}(R_1)}{\partial R_1} \cdot \left(\frac{\partial}{\partial r_{1\lambda}} \frac{\partial}{\partial r_{1\lambda'}} + \frac{\partial}{\partial p_{1\lambda'}} \frac{\partial}{\partial p_{1\lambda}} \right) \frac{\partial}{\partial P_1} W(t) \\
&\equiv i\mathcal{L}_m(x_1, X_1) W(t).
\end{aligned} \tag{21}
$$

Here the Wigner transform of the Hamiltonian (13) is given by

$$H_m = \frac{P^2}{2M} + V_B(R) + \sum_{\lambda\lambda'} \frac{h_{\lambda\lambda'}(R)}{2\hbar}(r_\lambda r_{\lambda'} + p_\lambda p_{\lambda'} - \hbar\delta_{\lambda\lambda'}). \tag{22}$$

This equation of motion is one of the principal results of this paper. It results from an expansion of the evolution operator for W to order μ and is equivalent to quantum-classical Liouville dynamics for the spectral density function [17]. The first term in Eq. (21) represents the subsystem dynamics of the spectral density in the mapping phase space. The second term is the dynamics of the spectral density due to classical evolution of the bath degrees of freedom and the third term is a higher order correlation between the quantum mapping and classical degrees of freedom. The last equality defines the quantum-classical Liouville operator in the mapping basis. This equation must be solved subject to the initial condition,

$$W(0) = (2\pi\hbar)^{(N_b+N)}\delta(r_1 - r_2)\delta(R_1 - R_2)\delta(p_1 - p_2)\delta(P_1 - P_2). \tag{23}$$

In Eq. (19), since $\hat{H}_m$ commutes with propagator $e^{i\hat{H}_m t}$, when differentiating with respect to time, $\hat{H}_m$ could be placed on either side of the propagator. In this derivation, we chose to put it to the left of the propagator in the first term in Eq. (19) and to the right of the propagator in the second term. If instead one places $\hat{H}_m$ to the right of the propagator in the first term and to the left of the propagator in the second term we can obtain an alternate form of the equation of motion[3]. The manipulations are similar to those described above and in the Appendix and are not repeated her. The resulting equation of motion is

$$
\begin{aligned}
\frac{\partial W(t)}{\partial t} &= +\frac{1}{\hbar}\sum_{\lambda\lambda'} h_{\lambda\lambda'}(R_2)\Big[r_{2\lambda}\frac{\partial}{\partial p_{2\lambda'}} - p_{2\lambda}\frac{\partial}{\partial r_{2\lambda'}}\Big]W(t) - \Big(\frac{P_2}{M}\cdot\frac{\partial}{\partial R_2} - \frac{\partial H_m}{\partial R_2}\cdot\frac{\partial}{\partial P_2}\Big)W(t) \\
&\quad -\frac{\hbar}{8}\sum_{\lambda\lambda'}\frac{\partial h_{\lambda\lambda'}(R_2)}{\partial R_2}\cdot\Big(\frac{\partial}{\partial r_{2\lambda}}\frac{\partial}{\partial r_{2\lambda'}} + \frac{\partial}{\partial p_{2\lambda'}}\frac{\partial}{\partial p_{2\lambda}}\Big)\frac{\partial}{\partial P_2}W(t) \\
&\equiv -i\mathcal{L}_m(x_2, X_2)W(t). \tag{24}
\end{aligned}
$$

This alternate form of the dynamics not only shows the symmetry of the dynamics of W in its variables but also allows us to move the time evolution from W to the observable B_{Wm} in the correlation function expression. The formal solution of Eq. (24) is

$$W(X_1, X_2, x_1, x_2, t) = e^{-i\mathcal{L}_m(x_2, X_2)t}W(X_1, X_2, x_1, x_2, 0). \tag{25}$$

These results will be used in the next section to derive a quantum-classical approximation to the time correlation function.

6   Quantum-Classical Correlation Function

We can now employ the results of the last two sections to find an expression for the quantum-classical approximation to the correlation function in the mapping basis. Using Eq. (25) in Eq. (16), we have

$$
\begin{aligned}
C_{AB}(t) &= \frac{1}{(2\pi\hbar)^{(N_b+N)}}\int dX_1 dX_2 dx_1 dx_2\ (\hat{\rho}_{eq}\hat{A})_{Wm}(X_1, x_1) \\
&\quad \times B_{Wm}(X_2, x_2)e^{-i\mathcal{L}_m(x_2, X_2)t}W(X_1, X_2, x_1, x_2, 0). \tag{26}
\end{aligned}
$$

---

[3]If $\hat{H}_m$ is placed in other locations, say, either to the right or left in both terms, the evolution operator for W is the mean of the two forms discussed in the text.

Performing an integration by parts to move the evolution operator onto the B_{Wm} and integrating over the coordinates with subscript 1, making use of the delta functions in the initial value of W, yields,

$$C_{AB}(t) \;\; = \;\; \int dX \, dx \, (\hat{\rho}_{eq} \hat{A})_{Wm}(X, x) B_{Wm}(X, x, t), \tag{27}$$

where $B_{Wm}(X, x, t) = e^{i\mathcal{L}_m(x,X)t} B_{Wm}(X, x)$. (We have dropped the subscripts on the phase space coordinates since this notation is no longer needed.) This expression contains the full quantum equilibrium structure of the subsystem and bath and the quantum-classical Liouville evolution of the operator $\hat{B}$ in the mapping representation.

The evolution equation for $B_{Wm}(X, x, t)$ that one obtains in this derivation is identical to that found earlier in the calculation of the average value of an observable [10]. This evolution equation can be written in the form

$$\frac{d}{dt} B_{Wm}(x, X, t) = i\mathcal{L}_m B_{Wm}(t) = -\{H_m, B_{Wm}(t)\}_{x,X} \tag{28}$$
$$+ \frac{\hbar}{8} \sum_{\lambda\lambda'} \frac{\partial h_{\lambda\lambda'}}{\partial R} \cdot \left(\frac{\partial}{\partial r_{\lambda'}} \frac{\partial}{\partial r_\lambda} + \frac{\partial}{\partial p_{\lambda'}} \frac{\partial}{\partial p_\lambda} \right) \frac{\partial}{\partial P} B_{Wm}(t),$$

where $\{\;,\;\}_{x,X}$ denotes a Poisson bracket in the full mapping-bath phase space of the system. The quantum-classical Liouville operator in the mapping basis can be decomposed into two terms, $i\mathcal{L}_m = i\mathcal{L}_m^0 + i\mathcal{L}_m'$ where

$$i\mathcal{L}_m^0 \;\; = \;\; -\{H_m, \quad \}_{x,X}, \tag{29}$$
$$i\mathcal{L}_m' \;\; = \;\; \frac{\hbar}{8} \sum_{\lambda\lambda'} \frac{\partial h_{\lambda\lambda'}}{\partial R} \cdot \left(\frac{\partial}{\partial r_{\lambda'}} \frac{\partial}{\partial r_\lambda} + \frac{\partial}{\partial p_{\lambda'}} \frac{\partial}{\partial p_\lambda} \right) \frac{\partial}{\partial P}.$$

The $i\mathcal{L}_m^0$ evolution operator, corresponding to the Poisson bracket in Eq. (28), leads to a classical-like evolution of the coupled dynamics of the quantum mapping and classical bath phase space variables that can be simulated by Newtonian trajectories. The force field that the classical variables feel varies with time as a result of the dependence of the forces on the mapping phase space variables. If $i\mathcal{L}_m'$ is dropped in the evolution equation, $B_{Wm}(t)$ has a solution in terms of characteristics. The set of ordinary differential equations that determines its solution is

$$\frac{dr_\lambda(t)}{dt} \;\; = \;\; \frac{1}{\hbar} \sum_{\lambda'} h_{\lambda\lambda'}(R(t)) p_{\lambda'}(t),$$
$$\frac{dp_\lambda(t)}{dt} \;\; = \;\; -\frac{1}{\hbar} \sum_{\lambda'} h_{\lambda\lambda'}(R(t)) r_{\lambda'}(t),$$
$$\frac{dR(t)}{dt} \;\; = \;\; \frac{P(t)}{M}, \quad \frac{dP(t)}{dt} = -\frac{\partial H_m}{\partial R(t)}. \tag{30}$$

The utility of this approximation to Eq. (28) is a topic of current research. Tests of its accuracy have been carried out on the spin-boson model where Eq. (28) is equivalent to full quantum dynamics and are being carried out on other model systems with nonlinear coupling between the quantum and classical degrees of freedom where Eq. (28) is not exact. For the spin-boson model Eq. (30) yields results that are indistinguishable from the known exact quantum results for this system [10]. Tests being carried out on other model systems show that while the results are often in close accord with exact quantum results, sometimes discrepancies are observed that cannot be ascribed to approximations in Eq. (28) for these more general interactions and must be attributed to the use of Eq. (30) for the dynamics. Consequently, further research is underway to fully characterize the contributions arising from $i\mathcal{L}_m'$ and construct algorithms that account for its action.

7   Conclusion

In the adiabatic basis the correlation function may be evaluated in terms of an ensemble of surface-hopping trajectories [3, 5]. While this simulation scheme has been used in a number of applications it is difficult to obtain accurate results for long times due the presence of oscillating terms in the Monte Carlo sampling. In this paper, we show that it is possible to reformulate the calculation of the correlation function in the mapping basis. Simulation schemes based on this formulation do not suffer from some of the problems that arise in the implementation of surface-hopping schemes.

In order to evaluate the expression for the correlation function obtained in this paper two ingredients are required. The expression involves an average over the full quantum equilibrium structure. As briefly discussed above, the computation of quantum equilibrium structure is a more tractable problem than the calculation of quantum dynamics. Nevertheless, approximations are usually required to evaluate the equilibrium structure. In the high temperature limit it is possible to derive analytical expressions that are useful in many applications [32, 33, 34].

The main result of this paper is the quantum-classical expression for the correlation function that involves time evolution of the quantum subsystem in the mapping basis. Provided the quantum-classical evolution is approximated by $i\mathcal{L}_m \simeq i\mathcal{L}_m^0$ the time evolution of the dynamical variable in the correlation function can be computed easily by solving a set of Newtonian-like equations. Thus, difficulties associated with the accumulation of Monte Carlo weights in the evaluation of an oscillatory function that arise in the surface-hopping solution of the quantum-classical Liouville equation in the adiabatic basis are by-passed. Of course, this simple scheme relies on the ability to neglect $i\mathcal{L}_m'$, which accounts for higher order correlations in the dynamics. Thus, the focus of future research is on the characterization of the nature of the dynamics generated by $i\mathcal{L}_m'$ and the construction of simulation algorithms that account for its presence. The results in this paper form the basis for future applications to the calculation of transport properties, such as rate constants for nonadiabtic chemical reactions.

Appendix: Derivation of the Dynamics

In this Appendix, we give the details of the calculations needed to obtain the quantum-classical evolution equation for the spectral density function. There are ten terms in Eq. (20) and, because of the symmetry of the expression, it is convenient to group term i with term i+5 and evaluate the contributions group by group. First, we perform the integrals over Q and q. The 1st and 6th terms contain $\frac{\partial^2}{\partial \tilde{Z}_1^2}$ and $\frac{\partial^2}{\partial \tilde{Z}_2^2}$, respectively, after this integration. Integration by parts with respect to $\tilde{Z}_1$ and $\tilde{Z}_2$ and summation of the results yield $\mu P_1 \cdot \frac{\partial W}{\partial R_1}$. The 2nd and 7th terms involve bath potentials. After expansion of $V_B(R_1 \pm \frac{\mu \tilde{Z}_1}{2})$ in μ, the first and third terms in the series, which are proportional to μ^0 and μ^2, cancel and the second terms, which are proportional to μ, yield $-\mu \frac{\partial V_B(R_1)}{\partial R_1} \cdot \frac{\partial W}{\partial P_1}$. The contribution from the 5th and 10th terms derived similarly to yield $\frac{\mu}{2} \frac{\partial \mathrm{Tr}(\mathbf{h})}{\partial R_1} \cdot \frac{\partial W}{\partial P_1}$. The derivations of the third and eighth and, also, forth and fifth groups of terms are more complicated and are presented in the following two subsections.

3rd and 8th terms:

The sum of the 3rd and 8th contributions to the time derivative of W is

$$
\left(\frac{\partial W}{\partial t}\right)_{3+8} = \frac{i\mu^{2N_b}}{2} \sum_{\lambda\lambda'} \int d\tilde{Z}_1 d\tilde{Z}_2 dz_1 dz_2 e^{-i(P_1\cdot\tilde{Z}_1 + P_2\cdot\tilde{Z}_2 + p_1\cdot z_1 + p_2\cdot z_2)}
$$
$$
\times\left\{\left[h_{\lambda\lambda'}(R_1) + \frac{\partial h_{\lambda\lambda'}(R_1)}{\partial R_1}\cdot\frac{\mu\tilde{Z}_1}{2}\right]\left[r_{1\lambda}r_{1\lambda'} + r_{1\lambda}z_{1\lambda'}/2 + z_{1\lambda}r_{1\lambda'}/2 + z_{1\lambda}z_{1\lambda'}/4\right]\right.
$$
$$
\left. -\left[h_{\lambda\lambda'}(R_1) - \frac{\partial h_{\lambda\lambda'}(R_1)}{\partial R_1}\cdot\frac{\mu\tilde{Z}_1}{2}\right]\left[r_{1\lambda}r_{1\lambda'} - r_{1\lambda}z_{1\lambda'}/2 - z_{1\lambda}r_{1\lambda'}/2 + z_{1\lambda}z_{1\lambda'}/4\right]\right\}
$$
$$
\times\langle r_1 + \frac{z_1}{2}|\langle R_1 + \frac{\mu\tilde{Z}_1}{2}|e^{i\hat{H}_m t}|R_2 - \frac{\mu\tilde{Z}_2}{2}\rangle|r_2 - \frac{z_2}{2}\rangle
$$
$$
\times\langle r_2 + \frac{z_2}{2}|\langle R_2 + \frac{\mu\tilde{Z}_2}{2}|e^{-i\hat{H}_m t}|R_1 - \frac{\mu\tilde{Z}_1}{2}\rangle|r_1 - \frac{z_1}{2}\rangle,
$$

where we have performed a McLauren expansion of $h_{\lambda\lambda'}$ in the small parameter μ, and retained the first two terms. Finally, using the fact that a partial differential with respect to momentum acting on the exponential term has the same effect as multiplication by the variable z_1 or $\tilde{Z}_1$ that results from the expansion, we have

$$
\left(\frac{\partial W}{\partial t}\right)_{3+8} = \frac{i\mu^{2N_b}}{2}\sum_{\lambda\lambda'}\int d\tilde{Z}_1 d\tilde{Z}_2 dz_1 dz_2\left\{ih_{\lambda\lambda'}(R_1)\left[r_{1\lambda}\frac{\partial}{\partial p_{1\lambda'}} + r_{1\lambda'}\frac{\partial}{\partial p_{1\lambda}}\right]\right.
$$
$$
\left. +\frac{\mu}{2}\frac{\partial h_{\lambda\lambda'}(R_1)}{\partial R_1}\cdot(i\frac{\partial}{\partial P_1})\left[2r_{1\lambda}r_{1\lambda'} - \frac{1}{2}\frac{\partial}{\partial p_{1\lambda}}\frac{\partial}{\partial p_{1\lambda'}}\right]\right\}e^{-i(P_1\cdot\tilde{Z}_1 + P_2\cdot\tilde{Z}_2 + p_1\cdot z_1 + p_2\cdot z_2)}
$$
$$
\times\langle r_1 + \frac{z_1}{2}|\langle R_1 + \frac{\mu\tilde{Z}_1}{2}|e^{i\hat{H}_m t}|R_2 - \frac{\mu\tilde{Z}_2}{2}\rangle|r_2 - \frac{z_2}{2}\rangle
$$
$$
\times\langle r_2 + \frac{z_2}{2}|\langle R_2 + \frac{\mu\tilde{Z}_2}{2}|e^{-i\hat{H}_m t}|R_1 - \frac{\mu\tilde{Z}_1}{2}\rangle|r_1 - \frac{z_1}{2}\rangle
$$
$$
= -\frac{1}{2}\sum_{\lambda\lambda'}h_{\lambda\lambda'}(R_1)\left[r_{1\lambda}\frac{\partial}{\partial p_{1\lambda'}} + r_{1\lambda'}\frac{\partial}{\partial p_{1\lambda}}\right]W
$$
$$
-\frac{\mu}{4}\sum_{\lambda\lambda'}\frac{\partial h_{\lambda\lambda'}(R_1)}{\partial R_1}\cdot\left[2r_{1\lambda}r_{1\lambda'} - \frac{1}{2}\frac{\partial}{\partial p_{1\lambda}}\frac{\partial}{\partial p_{1\lambda'}}\right]\frac{\partial}{\partial P_1}W,
$$

where in the last equality the expression for the scaled W is inserted.

4th and 9th terms:

The sum of the 4th and 9th terms in Eq. (20) is

$$\left(\frac{\partial W}{\partial t}\right)_{4+9} = -\frac{i\mu^{2N_b}}{2}\int d\tilde{Z}_1 d\tilde{Z}_2 dz_1 dz_2 \sum_{\lambda\lambda'}\left\{\left[h_{\lambda\lambda'}(R_1 + \frac{\mu\tilde{Z}_1}{2})\frac{\partial}{\partial(r_1 + \frac{z_1}{2})_\lambda}\frac{\partial}{\partial(r_1 + \frac{z_1}{2})_{\lambda'}}\right.\right.$$

$$\times \langle r_1 + \frac{z_1}{2}|\langle R_1 + \frac{\mu\tilde{Z}_1}{2}|e^{i\hat{H}_m t}|R_2 - \frac{\mu\tilde{Z}_2}{2}\rangle|r_2 - \frac{z_2}{2}\rangle\Big]$$

$$\times \langle r_2 + \frac{z_2}{2}|\langle R_2 + \frac{\mu\tilde{Z}_2}{2}|e^{-i\hat{H}_m t}|R_1 - \frac{\mu\tilde{Z}_1}{2}\rangle|r_1 - \frac{z_1}{2}\rangle$$

$$-\Big[h_{\lambda\lambda'}(R_1 - \frac{\mu\tilde{Z}_1}{2})\frac{\partial}{\partial(r_1 - \frac{z_1}{2})_\lambda}\frac{\partial}{\partial(r_1 - \frac{z_1}{2})_{\lambda'}}$$

$$\times \langle r_2 + \frac{z_2}{2}|\langle R_2 + \frac{\mu\tilde{Z}_2}{2}|e^{-i\hat{H}_m t}|R_1 - \frac{\mu\tilde{Z}_1}{2} > |r_1 - \frac{z_1}{2}\rangle\Big]$$

$$\left.\times \langle r_1 + \frac{z_1}{2}|\langle R_1 + \frac{\mu\tilde{Z}_1}{2}|e^{i\hat{H}_m t}|R_2 - \frac{\mu\tilde{Z}_2}{2}\rangle|r_2 - \frac{z_2}{2}\rangle\right\}e^{-i(P_1\cdot\tilde{Z}_1 + P_2\cdot\tilde{Z}_2 + p_1\cdot z_1 + p_2\cdot z_2)}$$

$$= -\frac{i\mu^{2N_b}}{2}\sum_{\lambda\lambda'}\int d\tilde{Z}_1 d\tilde{Z}_2 dz_1 dz_2\left\{\left[\left(h_{\lambda\lambda'}(R_1) + \frac{\partial h_{\lambda\lambda'}(R_1)}{\partial R_1}\frac{\mu\tilde{Z}_1}{2}\right)\right.\right.$$

$$\left.\times \frac{\partial}{\partial r_{1\lambda}}\frac{\partial}{\partial r_{1\lambda'}}\langle r_1 + \frac{z_1}{2}|\langle R_1 + \frac{\mu\tilde{Z}_1}{2}|e^{i\hat{H}_m t}|R_2 - \frac{\mu\tilde{Z}_2}{2}\rangle|r_2 - \frac{z_2}{2}\rangle\right]$$

$$\times \langle r_2 + \frac{z_2}{2}|\langle R_2 + \frac{\mu\tilde{Z}_2}{2}|e^{-i\hat{H}_m t}|R_1 - \frac{\mu\tilde{Z}_1}{2}\rangle|r_1 - \frac{z_1}{2}\rangle$$

$$-\Big[\left(h_{\lambda\lambda'}(R_1) - \frac{\partial h_{\lambda\lambda'}(R_1)}{\partial R_1}\frac{\mu\tilde{Z}_1}{2}\right)$$

$$\left.\times \frac{\partial}{\partial r_{1\lambda}}\frac{\partial}{\partial r_{1\lambda'}}\langle r_2 + \frac{z_2}{2}|\langle R_2 + \frac{\mu\tilde{Z}_2}{2}|e^{-i\hat{H}_m t}|R_1 - \frac{\mu\tilde{Z}_1}{2}\rangle|r_1 - \frac{z_1}{2}\rangle\right]$$

$$\left.\times \langle r_1 + \frac{z_1}{2}|\langle R_1 + \frac{\mu\tilde{Z}_1}{2}|e^{i\hat{H}_m t}|R_2 - \frac{\mu\tilde{Z}_2}{2}\rangle|r_2 - \frac{z_2}{2}\rangle\right\}e^{-i(P_1\cdot\tilde{Z}_1 + P_2\cdot\tilde{Z}_2 + p_1\cdot z_1 + p_2\cdot z_2)}. \tag{31}$$

Again in the second equality we have carried out a McLauren expansion of $h_{\lambda\lambda'}$ to first order in μ. Equation (31) itself has four terms. In the sum of the 1st and 3rd subcontributions one of the partial derivatives over r may be replaced by a partial derivative over z and an integration by parts may be

carried out. We find

$$\frac{i\mu^{2N_b}}{2}\sum_{\lambda\lambda'}h_{\lambda\lambda'}(R_1)\int d\tilde{Z}_1 d\tilde{Z}_2 dz_1 dz_2 e^{-i(P_1\cdot\tilde{Z}_1+P_2\cdot\tilde{Z}_2+p_1\cdot z_1+p_2\cdot z_2)}$$

$$\times\left\{\left[2\frac{\partial}{\partial r_{1\lambda'}}\langle r_1+\frac{z_1}{2}|\langle R_1+\frac{\mu\tilde{Z}_1}{2}|e^{i\hat{H}_m t}|R_2-\frac{\mu\tilde{Z}_2}{2}\rangle|r_2-\frac{z_2}{2}\rangle\right.\right.$$

$$\left.\times(\frac{\partial}{\partial z_{1\lambda}}-ip_{1\lambda})\langle r_2+\frac{z_2}{2}|\langle R_2+\frac{\mu\tilde{Z}_2}{2}|e^{-i\hat{H}_m t}|R_1-\frac{\mu\tilde{Z}_1}{2}\rangle|r_1-\frac{z_1}{2}\rangle\right]$$

$$-\left[(-2)\frac{\partial}{\partial r_{1\lambda'}}\langle r_2+\frac{z_2}{2}|\langle R_2+\frac{\mu\tilde{Z}_2}{2}|e^{-i\hat{H}_m t}|R_1-\frac{\mu\tilde{Z}_1}{2}\rangle|r_1-\frac{z_1}{2}\rangle\right.$$

$$\left.\left.\times(\frac{\partial}{\partial z_{1\lambda}}-ip_{1\lambda})\langle r_1+\frac{z_1}{2}|\langle R_1+\frac{\mu\tilde{Z}_1}{2}|e^{i\hat{H}_m t}|R_2-\frac{\mu\tilde{Z}_2}{2}\rangle|r_2-\frac{z_2}{2}\rangle\right]\right\}$$

$$=\sum_{\lambda\lambda'}h_{\lambda\lambda'}(R_1)p_{1\lambda}\frac{\partial}{\partial r_{1\lambda'}}W. \tag{32}$$

Here we see that the two terms with a momentum multiplier are added together while the other terms cancel each other.

The 2nd and 4th subcontributions in Eq. (31) are treated in the following way: We replace multiplication by the variable $\tilde{Z}$ with a partial differentiation with respect to the momentum. Furthermore, the sum of these contributions is written as one half the sum of two equal contributions, the expressions appearing in Eq. (31) and the same expression but with the differentials over r replaced with those over z. Thus, the sum of the 2nd and 4th contributions can be written as

$$-\frac{i\mu^{2N_b+1}}{8}\sum_{\lambda\lambda'}\frac{\partial h_{\lambda\lambda'}(R_1)}{\partial R_1}\int d\tilde{Z}_1 d\tilde{Z}_2 dz_1 dz_2(i\frac{\partial}{\partial P_1})e^{-i(P_1\cdot\tilde{Z}_1+P_2\cdot\tilde{Z}_2+p_1\cdot z_1+p_2\cdot z_2)}$$

$$\times\left\{\left[\left(\frac{\partial}{\partial r_{1\lambda}}\frac{\partial}{\partial r_{1\lambda'}}\langle r_1+\frac{z_1}{2}|\langle R_1+\frac{\mu\tilde{Z}_1}{2}|e^{i\hat{H}_m t}|R_2-\frac{\mu\tilde{Z}_2}{2}\rangle|r_2-\frac{z_2}{2}\rangle\right)\right.\right.$$

$$\times\langle r_2+\frac{z_2}{2}|\langle R_2+\frac{\mu\tilde{Z}_2}{2}|e^{-i\hat{H}_m t}|R_1-\frac{\mu\tilde{Z}_1}{2}\rangle|r_1-\frac{z_1}{2}\rangle$$

$$+\langle r_1+\frac{z_1}{2}|\langle R_1+\frac{\mu\tilde{Z}_1}{2}|e^{i\hat{H}_m t}|R_2-\frac{\mu\tilde{Z}_2}{2}\rangle|r_2-\frac{z_2}{2}\rangle$$

$$\left.\times\left(\frac{\partial}{\partial r_{1\lambda}}\frac{\partial}{\partial r_{1\lambda'}}\langle r_2+\frac{z_2}{2}|\langle R_2+\frac{\mu\tilde{Z}_2}{2}|e^{-i\hat{H}_m t}|R_1-\frac{\mu\tilde{Z}_1}{2}\rangle|r_1-\frac{z_1}{2}\rangle\right)\right]$$

$$+4\left[\left(\frac{\partial}{\partial z_{1\lambda}}\frac{\partial}{\partial z_{1\lambda'}}\langle r_1+\frac{z_1}{2}|\langle R_1+\frac{\mu\tilde{Z}_1}{2}|e^{i\hat{H}_m t}|R_2-\frac{\mu\tilde{Z}_2}{2}\rangle|r_2-\frac{z_2}{2}\rangle\right)\right.$$

$$\times\langle r_2+\frac{z_2}{2}|\langle R_2+\frac{\mu\tilde{Z}_2}{2}|e^{-i\hat{H}_m t}|R_1-\frac{\mu\tilde{Z}_1}{2}\rangle|r_1-\frac{z_1}{2}\rangle$$

$$+\langle r_1+\frac{z_1}{2}|\langle R_1+\frac{\mu\tilde{Z}_1}{2}|e^{i\hat{H}_m t}|R_2-\frac{\mu\tilde{Z}_2}{2}\rangle|r_2-\frac{z_2}{2}\rangle$$

$$\left.\left.\times\left(\frac{\partial}{\partial z_{1\lambda}}\frac{\partial}{\partial z_{1\lambda'}}\langle r_2+\frac{z_2}{2}|\langle R_2+\frac{\mu\tilde{Z}_2}{2}|e^{-i\hat{H}_m t}|R_1-\frac{\mu\tilde{Z}_1}{2}\rangle|r_1-\frac{z_1}{2}\rangle\right)\right]\right\}. \tag{33}$$

If in both expressions we replace $\frac{\partial^2 A}{\partial x\partial y}B+A\frac{\partial^2 B}{\partial x\partial y}$ with $\frac{\partial^2(AB)}{\partial x\partial y}-\frac{\partial A}{\partial x}\frac{\partial B}{\partial y}-\frac{\partial A}{\partial y}\frac{\partial B}{\partial x}$, the cross terms cancel.

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Finally, integrating by parts over $z_{1\lambda}$ and $z_{1\lambda'}$, we get

$$\frac{\mu}{8} \sum_{\lambda\lambda'} \frac{\partial h_{\lambda\lambda'}(R_1)}{\partial R_1} \cdot \left(\frac{\partial}{\partial r_{1\lambda}} \frac{\partial}{\partial r_{1\lambda'}} - 4p_{1\lambda}p_{1\lambda'}\right) \frac{\partial}{\partial P_1} W. \tag{34}$$

Summing all the contributions from the above calculations, we find the comparatively simple result

$$\begin{aligned}
\frac{\partial W}{\partial t} &= -\sum_{\lambda\lambda'} h_{\lambda\lambda'}(R_1)\left[r_{1\lambda}\frac{\partial}{\partial p_{1\lambda'}} - p_{1\lambda}\frac{\partial}{\partial r_{1\lambda'}}\right]W \\
&\quad + \mu P_1 \cdot \frac{\partial W}{\partial R_1} - \mu \frac{\partial V_B(R_1)}{\partial R_1} \cdot \frac{\partial W}{\partial P_1} - \frac{\mu}{2}\sum_{\lambda\lambda'}\frac{\partial h_{\lambda\lambda'}(R_1)}{\partial R_1} \cdot (r_{1\lambda}r_{1\lambda'} + p_{1\lambda}p_{1\lambda'} - \delta_{\lambda\lambda'})\frac{\partial}{\partial P_1}W \\
&\quad + \frac{\mu}{8}\sum_{\lambda\lambda'}\frac{\partial h_{\lambda\lambda'}(R_1)}{\partial R_1} \cdot \left(\frac{\partial}{\partial r_{1\lambda}}\frac{\partial}{\partial r_{1\lambda'}} + \frac{\partial}{\partial p_{1\lambda}}\frac{\partial}{\partial p_{1\lambda'}}\right)\frac{\partial}{\partial P_1}W.
\end{aligned} \tag{35}$$

Restoring unscaled coordinates we have Eq. (21) in the text.

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